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Reduction Activation of Addition Polymerization

By T. E. STANIN*

Certain types of unsaturated compounds are capable of polymerizing to high molecular weights by a chain reaction mechanism which involves a carbon-carbon double bond (1). Compounds such as ethylene, vinyl chloride, vinyl esters, styrene, acrylic acid and its esters, etc., contain such a double bond.

The activation of the double bond involves the formation of a free radical by some means (e.g., decomposition of peroxide or absorption of radiant energy). The free radical, M*, then adds to the double bond of the polymerizable compound or monomer:

$$M^* + CH_2 = CHX \longrightarrow MCH_2 - \underset{\displaystyle X}{\underset{|}{CH}}\cdot$$

The process is repeated by successive additions to monomer,

$$M - CH_2 - \underset{\displaystyle X}{\underset{|}{CH}}\cdot + n(CH_2 = CHX) \longrightarrow M(CH_2 - \underset{\displaystyle X}{\underset{|}{CH}})_n - CH_2 - \underset{\displaystyle X}{\underset{|}{CH}}\cdot ,$$

until the growing chain is deactivated by collision with some molecule (N) to which it transfers its activity:

$$M(CH_2 - \underset{\displaystyle X}{\underset{|}{CH}})_nCH_2 - \underset{\displaystyle X}{\underset{|}{CH}}\cdot + N \longrightarrow M(CH_2 - CHX)_nCH_2 - \underset{\displaystyle X}{\underset{|}{CH_2}} + N^*$$

In this process, N usually gives up a hydrogen or a halogen to the polymer molecule.

The growing chain may also be deactivated by coupling with another active radical,

$$R_1^* + R_2^* \longrightarrow R_1 - R_2 ,$$

or by disproportionation:

$$M(CH_2 - \underset{\displaystyle X}{\underset{|}{CH}})_nCH_2 - \underset{\displaystyle X}{\underset{|}{CH}}\cdot + \cdot\underset{\displaystyle X}{\underset{|}{CH}} - CH_2(CH - CH_2)_nM \longrightarrow M(CH_2 - \underset{\displaystyle X}{\underset{|}{CH}})_n - CH = CHX + \underset{\displaystyle X}{\underset{|}{CH_2}} - CH_2(\underset{\displaystyle X}{\underset{|}{CH}} - CH_2)_nM .$$

Unless precautions are taken to insure the purity of the materials that are mixed in a polymerization reaction, a certain length of time is required before the reaction begins. The time required is commonly referred to as the "induction period" and is generally caused by the presence of impurities which inhibit the reaction by reacting preferentially with the free radicals that are first formed.

Recent patent literature indicates that efforts have been made to accelerate polymerization reactions by the use of activators in addition to the usual

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initiators used. Pfau (2) has used potassium ferricyanide with potassium persulfate in the emulsion polymerization of 1,3-butadiene. Stewart (3) has used water-soluble heavy metal salts together with aliphatic polycarboxylic acids as activators for polymerizations initiated by hydrogen peroxide. In another patent (4), he has disclosed the use of α-amino acids with the salts. Fryling (5) has used sodium pyrophosphate, sodium oxalate, potassium fluoride, urea, glycine, alanine, etc., to activate polymerization initiated by hydrogen peroxide. Gumlich (6) has found that water-soluble, heavy metal phthalocyanine complexes capable of existing in different states of oxidation (particularly iron phthalocyanine sulfonic acid) activate polymerization of 1,3-butadienes in aqueous emulsion initiated by oxygen, peroxides, or persulfates.

Persulfates

In a series of studies on acrylonitrile in aqueous solution, Bacon (7) has found that polymerization initiated by persulfates is greatly accelerated by the presence of reducing agents. The most effective activators were found to be organic sulfides, hydrogen sulfide, oxyacids of sulfur that possess reducing properties, and the salts of these acids. Silver nitrate also showed great efficiency, and metals such as copper, iron, and silver were effective, particularly if their surface area was large.

The conditions chosen for the experiments were such that in the absence of an activator a yield of 1.5 per cent of polymer was obtained in 60 minutes and the induction period was 30 minutes. The activators varied in efficiency from one to fifty times. The most efficient ones reduced the induction period to zero and raised the yield to more than 80 per cent in 60 minutes. The effectiveness of the activators differed with different monomers. Thus, a very efficient activator for one monomer might show altogether different activity with another monomer.

Oxygen had an inhibiting effect on the polymerization with a persulfate-bisulfite system. The induction period varied according to the amount of oxygen present, the temperature, and the catalyst concentration. Once the polymerization started, however, little effect on the rate by any of these was observed, except when undiluted oxygen was used. The removal of oxygen from the system by the reducing agent did not account for the activation. The activation appeared to be caused by the interaction of the reducing agent and the initiator. The course of the polymerization depended on the duration of the reaction between initiator and activator. The addition product of sodium bisulfite and acrylonitrile had no influence on the course of the reaction.

The pH of the sodium sulfite-persulfate system increased as the reaction progressed, possibly as a result of the following reaction:

$$CH_2 = CHCN + Na_2SO_3 + H_2O \longrightarrow CH_2(SO_3Na)CH_2CN + NaOH \ .$$

Although the initial pH had little effect on the unactivated persulfate polymerization in the range between 3 and 11, the bisulfite-activated polymerization was greatly affected. The yield dropped from between 80 and 90 per cent to 2 per cent when the initial pH was above 6, except in the case of vinyl chloride in emulsion, where little difference was observed.

The nature of the initiating species resulting from the reaction of thiosulfate and persulfate is still unknown, according to Morgan (8).

Hydrogen Peroxide

Certain metallic ions capable of being oxidized to a higher valence state were found to activate polymerizations initiated by hydrogen peroxide in aqueous solution or in emulsion (9). Chromous, mercurous, cuprous, titanous, manganous, and ferrous ions were found to be effective, and the mechanism of activation appears to be clearer.

The decomposition of hydrogen peroxide in the presence of ferrous ions was outlined by Haber and Weiss (10):

1. $H_2O_2 + Fe^{++} \longrightarrow HO\cdot + HO^- + Fe^{+++}$
2. $HO\cdot + Fe^{++} \longrightarrow HO^- + Fe^{+++}$
3. $HO\cdot + H_2O_2 \longrightarrow H_2O + HO_2\cdot$
4. $\begin{cases} HO_2\cdot + H_2O_2 \longrightarrow HO\cdot + O_2 + H_2O \\ HO_2\cdot \rightleftharpoons O_2^- + H^+ \\ O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + HO\cdot \end{cases}$.

In excess hydrogen peroxide, oxygen is evolved by virtue of steps 3 and 4. Baxendale, Evans, and Park (9) found that in excess hydrogen peroxide and monomer, polymerization occurred immediately and no oxygen was evolved. The following outline has been proposed as the most probable mechanism in the presence of monomer:

I. $H_2O_2 + Fe^{++} \longrightarrow HO\cdot + HO^- + Fe^{+++}$

II. $HO\cdot + Fe^{++} \longrightarrow HO^- + Fe^{+++}$

III. $HO\cdot + CH_2{=}CH \longrightarrow HOCH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H\cdot$

IV. $HOCH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H\cdot + CH_2{=}\underset{\displaystyle X}{\underset{|}{C}}H \longrightarrow HOCH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H\cdot$.

With excess ferrous ions and in the absence of monomer, steps I and II are predominant. In the presence of excess monomer, step II is suppressed and step III leading to polymer formation is predominant. Step III was found to be about five times as fast as step II. Termination of the growing polymer chains by hydroxyl radicals was also suggested.

The reaction was found to absorb oxygen and to be inhibited by this process. The amount of oxygen absorbed was found by measurement to be comparable to the concentration of hydroxyl radicals reacting with the monomer. More ferrous ions were oxidized in the presence of oxygen than in its absence, which led to the suggestion that oxygen participates in chain termination by the following process:

$$HO(CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H)_n\cdot + O_2 \longrightarrow HO(CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H)_n{-}O{-}O\cdot$$

$$HO(CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H)_{n-1}{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H{-}O{-}O\cdot + Fe^{++} \longrightarrow HO(CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}H)_{n-1}{-}CH_2{-}\underset{\displaystyle X}{\underset{|}{C}}{=}O + OH^- + Fe^{+++}.$$

This would account for the increase in the number of ferric ions in the presence of oxygen.

Vandenberg and Hulse (11) reported that cumene hydroperoxide, activated by a reducing agent such as fructose, with a soluble iron salt such as ferrous or ferric pyrophosphate, gave a ten- to twentyfold increase in the polymerization rates of a number of different vinyl compounds, when emulsified with a disproportionated rosin soap such as Dresinol 731.

The rate of polymerization was linear and depended on the fructose concentration. The iron salt eliminated the initial periods of slow polymerization.

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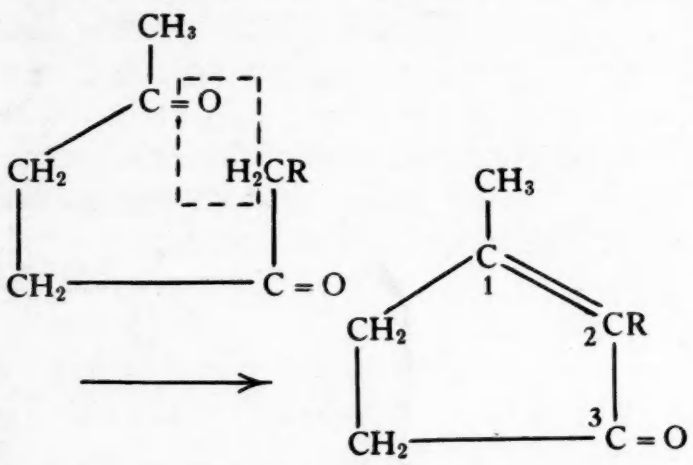
A New Synthesis of Cyclopentenones

By C. F. H. ALLEN*

SINCE the discovery that jasmone, the ketone occurring in oil of jasmine, is a substituted cyclopentenone, practical methods of preparation for this class of compounds have been sought. A few isolated syntheses have long been known, but within the last decade, largely through the work of Hunsdiecker, a general reaction has been discovered.

This synthesis is essentially an aldol type of intramolecular condensation of saturated 1,4-diketones. The previous nonavailability of these diketones was the main reason for delay in application of this reaction.

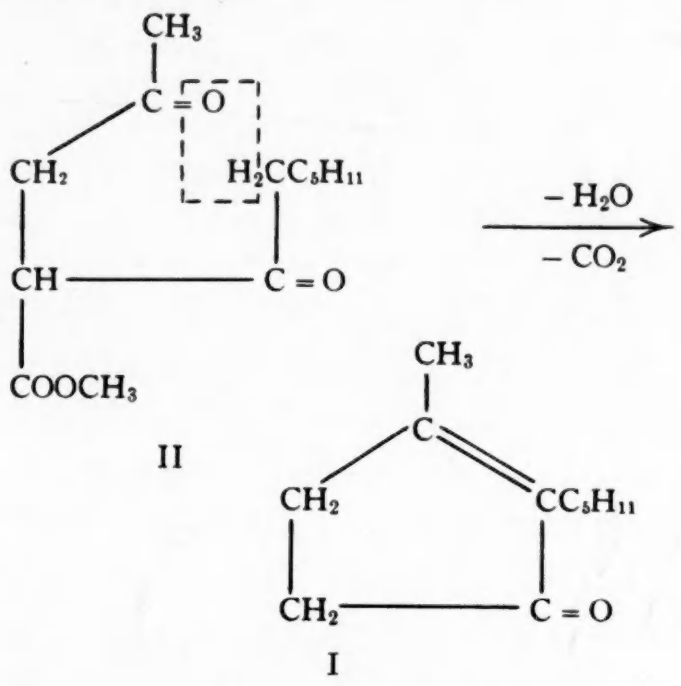
This condensation, which is catalyzed by hydroxyl ion, is very rapid, and the yields are high. It may be represented as follows:



It might be expected that unsymmetrical diketones would give two products; however, a methyl group attached to the carbonyl carbon atom does not take part in the condensation. The single product is always a methylcyclopentenone.

The reaction appears to be general. The only exception so far discovered is acetonylacetone, the first and longest known member of the diketone series.

Both dihydrojasmone (1-methyl-2-*n*-amylcyclopenten-3-one, [I, below]) and jasmone have been obtained by application of this cyclization. In these instances it is not necessary to isolate a 1,4-diketone, but the corresponding α-acyl levulinic ester, II, serves as the starting material. For instance, if *n*-heptoyl chloride is used to acylate the acetoacetic ester (as outlined in the previous article on 1,4-diketones), the desired cyclopentenone (dihydrojasmone) can be obtained in one step.



II

I

It should be noted that the water, eliminated in the condensation, hydrolyzes the ester to the free acid, which is then decarboxylated. By a very ingenious method, the ester group can be retained in the molecule (but the cyclic ester is odorless); an ester, such as methyl or ethyl acetate, which can be easily hydrolyzed, is added to the reaction mixture. The added ester then undergoes a preferential hydrolysis, using up the water, to form an alcohol and sodium acetate. This manipulative procedure should be applicable to other condensation reactions, in which the water produced must be eliminated to avoid side reactions.

These cyclopentenones have already found a place in the perfume industry, and other applications will undoubtedly be discovered.

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